

In-gap state and effect of light illumination in CuIr_2S_4 probed by photoemission spectroscopy

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Abstract

We have studied disorder-induced in-gap states and effect of light illumination in the insulating phase of spinel-type CuIr_2S_4 using ultra-violet photoemission spectroscopy (UPS). The $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge-ordered gap appears below the metal-insulator transition temperature. However, in the insulating phase, in-gap spectral features with *softgap* are observed in UPS just below the Fermi level (E_F), corresponding to the variable range hopping transport observed in resistivity. The spectral weight at E_F is not increased by light illumination, indicating that the $\text{Ir}^{4+}\text{-Ir}^{4+}$ dimer is very robust although the long-range octamer order would be destructed by the photo-excitation. Present results suggest that the $\text{Ir}^{4+}\text{-Ir}^{4+}$ bipolaronic hopping and disorder effects are responsible for the conductivity of CuIr_2S_4 .

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I. INTRODUCTION

When some disorders are introduced in Mott insulators or charge-ordered insulators, disorder-induced electronic states are often observed within the band gaps and are responsible for the hopping transport in the insulating phase. [1, 2, 3, 4] Although it is very important to understand the relationship between the transport behaviors and the disorder-induced in-gap states, no unified picture on the relationship is obtained so far. For example, in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, [1] $\text{NiS}_{2-x}\text{Se}_x$, [2] and $\text{R}_{1-x}\text{A}_x\text{MnO}_3$, [3] almost localized electronic states are formed within the band gap and are responsible for the variable range hopping (VRH) transport. On the other hand, in lightly-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.03$), a sharp peak with clear band dispersion is observed within the Mott gap while the resistivity shows a VRH behavior. [4] The VRH transports and in-gap states suggest that the insulating and metallic clusters coexist near the metal-insulator transition (MIT) in these materials. [5, 6] Such inhomogeneity plays crucial roles in their remarkable properties of colossal magnetoresistance and photo-induced MIT in manganites, [7, 8] and stripe formation in cuprates. [9]

CuIr_2S_4 with spinel structure is one of such systems and shows a MIT at $T_{MI} \sim 226\text{K}$. [10, 11, 12, 13, 14, 15, 16] The anomalous hopping transport is also observed in the insulating phase $\rho \propto \exp[-(T/T_0)^{1/2}]$, [17, 18] or $\rho \propto A\exp(-E_a/k_B T) + B\exp[-(T/T_0)^{1/4}]$. [19, 20] The temperature variation of $\rho \propto \exp[-(T/T_0)^{1/2}]$ can be described by a Mott VRH conductivity in one dimensional case [21] or by a Efros-Shklovskii VRH conductivity. [22] However, a rather complicated three dimensional charge ordering of Ir^{3+} ($S=0$) and Ir^{4+} ($S=1/2$) sites are indicated in the insulating phase of CuIr_2S_4 . [23] The cubic spinel structure of CuIr_2S_4 becomes tetragonally elongated along the c -axis and bi-capped hexagonal ring octamers of Ir^{3+} and Ir^{4+} are formed below T_{MI} . The orbital driven Peierls mechanism has been suggested, [24] in which the Ir^{4+} ions are dimerized along xy chains of the B -sites. Moreover, the resistivity of CuIr_2S_4 is reduced by x-ray, [25, 26] visible light, [27, 28] or electron beam irradiation [29, 30] at low temperature ($\sim 100\text{ K}$). The symmetry of crystal is changed from triclinic to tetragonal by the irradiation and the photo-induced state has a long lifetime. It has been proposed that the photo-excitation breaks the $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge ordering and induces the metallic conductivity.

The indication of MIT and the $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge ordering has been obtained on previous x-ray photoemission and absorption studies of CuIr_2S_4 . [27, 31, 32, 33, 34, 35] The Ir 4f

core-level spectrum of the insulating phase has two components with large energy difference, consistent with the charge ordering of Ir sites. [27, 35] In contrast, the core-level spectrum has not been changed against laser irradiation, while the resistivity is reduced.

In this article, we report results of ultra-violet photoemission spectroscopy (UPS) of CuIr_2S_4 single crystals combined with laser illumination. The UPS spectrum shows a clear MIT with band-gap opening ~ 0.09 eV. However, the UPS spectrum just below the Fermi level (E_F) at low temperature (~ 20 K) has a peculiar power-law dependence $\sim (E - E_F)^n$, $n \sim 1.3 - 1.7$, that is associated with the anomalous conduction. The systematic spectral change of UPS against laser irradiation has not been observed. The Ir^{4+} - Ir^{4+} dimers in the xy plane of spinel are very robust against photo-excitation and play important roles in the exotic conduction.

II. EXPERIMENTS

Single crystals of CuIr_2S_4 were grown by the bismuth solution method, described previously in detail. [36] UPS measurements were performed using SCIENTA SES-100 spectrometers equipped with a He I source ($h\nu = 21.2$ eV). The total resolution was 30 meV and the base pressure of the spectrometer was 1×10^{-7} Pa. Five CuIr_2S_4 single crystals were studied for UPS measurements. The first and second samples named $\#R1$ and $\#R2$ are cleaved at 300 K *in situ* and then measured at various temperatures. The third, fourth, and fifth samples named $\#L3$, $\#L4$, and $\#L5$ are cleaved at 20 K *in situ* and then measured at various temperatures. All photoemission data were collected within 24 hours after the cleaving. In order to study the effects of visible light excitation, a Nd:YAG pulsed laser provided optical excitation to the samples at energies of 2.3 eV (532 nm) with a pulse frequency of 30 Hz and a pulse width of about 10 ns. The beam was focused to a spot of 4 mm diameter.

III. RESULTS AND DISCUSSIONS

A. Temperature dependence

Figure 1 shows wide-range UPS of CuIr_2S_4 taken at 300 K for sample $\#R1$ and 20 K for sample $\#L3$ immediately after cleaving, respectively. Compared with the previous studies, [27, 31, 32, 37, 38] structures A, B, and C are assigned to the Ir 5d-S 3p antibonding

band, the Cu 3d band, and Ir 5d-S 3p bonding band, respectively. In the near- E_F spectra, a spectral change across the MIT is observed. The intensity at E_F is substantial in the spectrum at 300 K (sample #R1, red line, metallic phase), while the intensity at E_F almost disappears in the spectrum at 20 K (sample #L3, blue line, insulating phase) [See Fig. 1 (b)]. The opening of the gap $E_{gap} \sim 0.09$ eV, obtained by extrapolating the slope near the valance-band maximum to the base line, agrees with the previous photoemission results [16, 27, 35] and is attributed to the Ir³⁺/Ir⁴⁺ charge ordering and Ir⁴⁺-Ir⁴⁺ dimerization along the xy chains with the tetragonal distortion.

The spectrum of the insulating phase has a tail above the valence-band maximum that reaches E_F and forms a kind of *softgap*, interestingly. This observation directly corresponds to the anomalous hopping transport observed in the resistivity measurements $\rho \propto \exp[-(T/T_0)^{1/2}]$, [17, 18] or $\rho \propto A\exp(-E_a/k_B T) + B\exp[-(T/T_0)^{1/4}]$. [19, 20] We have fitted this in-gap spectral feature up to 0.09 eV ($\sim E_{gap}$) to two types of model functions $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_F}{\sqrt{2}C})^2]$ and $A(E - E_0)^n$ (Fig. 2). The power-law function $A(E - E_F)^n$ is additionally convoluted with a gaussian function taking into account the instrumental and thermal broadenings (~ 40 meV). The gaussian peak $\frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_F}{\sqrt{2}C})^2]$ is assumed to be a contribution from surface residual bonds near E_F and it will be discussed later. The integrated intensity is normalized to unity and the fitted parameters are shown in Table I. The exponent of n for sample #L3 is estimated to be ~ 1.5 and ~ 1.7 by using the functions of $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_F}{\sqrt{2}C})^2]$ and $A(E - E_0)^n$, respectively.

Temperature dependence of the wide-range UPS was carefully examined for various fractured surfaces. Figure 3 (a) shows temperature dependence of UPS for sample #R1, which was cleaved at 300 K and then measured with decreasing temperature. Although the spectra show the band-gap opening, a hump structure near E_F remains even at the lowest temperature ~ 20 K in contrast to the spectra for sample #L3 measured immediately after cleaving at 20 K. Sample #R2 was also cleaved at 300 K and then measured with decreasing temperature. However on the spectrum immediately taken after cooling down, such hump is almost absent [Fig. 3 (b) blue line]. Moreover after keeping 20 K for 30 minutes, the intense hump (green line) appeared also for this sample #R2. Even for sample #L3, cleaved at low temperature, the intensity gradually increased with time although the intensity is rather small compared to the samples cleaved at 300K (#R1, #R2). Even at 20 K, the intensity of the hump depends on the cleavage. While, for sample #L4 cleaved at 20 K, the hump

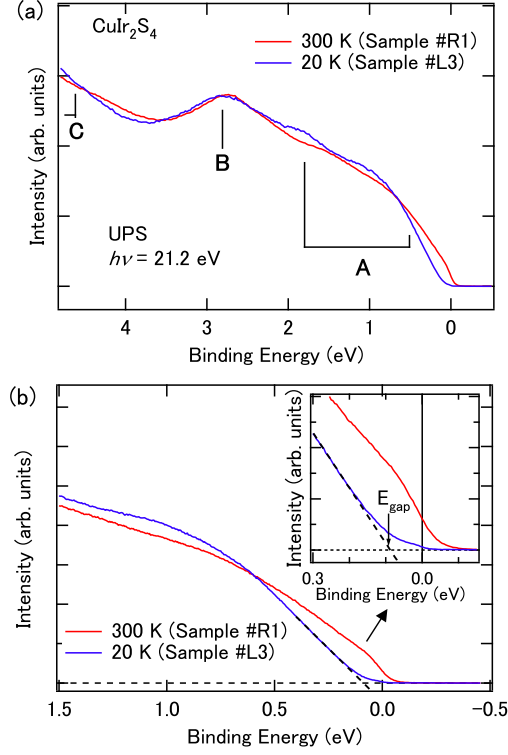


FIG. 1: (Color online) UPS of CuIr_2S_4 taken at 300 K and 20 K immediately after cleaving. (a) Wide-range spectra. (b) Near- E_F spectra. Inset of (b) shows the expanded spectra near E_F .

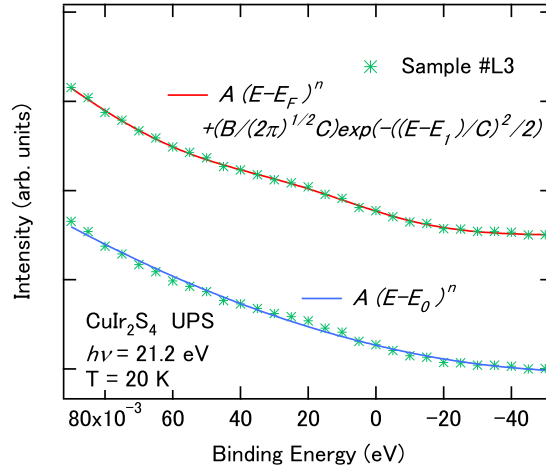


FIG. 2: (Color online) UPS of CuIr_2S_4 for sample #L3 taken at 20 K immediately after cleaving. The solid curves indicate the fitted results with model functions $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C} \exp[-(\frac{E - E_1}{\sqrt{2}C})^2]$ and $A(E - E_0)^n$, respectively.

TABLE I: Best fit parameters of the model functions $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_1}{\sqrt{2}C})^2]$ and $A(E - E_0)^n$ for the spectra of sample #L3 of CuIr₂S₄. The spectra are normalized using integrated intensity up to 0.09 eV.

Function : $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_1}{\sqrt{2}C})^2]$				
Sample (20 K)	n	B	C (eV)	E_1 (eV)
#L3	1.5 ± 0.2	0.23 ± 0.03	0.02 ± 0.01	0.02 ± 0.01

Function : $A(E - E_0)^n$				
Sample (20 K)	n	B	C (eV)	E_1 (eV)
#L3	1.7 ± 0.2	-	-	-

was clearly observed, its intensity was very small for sample #L5. The hump structure is probably due to the surface state composed of unpaired Ir⁴⁺ at the surface. Thus the hump structure can be affected by various surface conditions including treatments such as cleaving, change of temperature or irradiation from He I source. We have tried to fit all the spectra taken at 20 K with the function $A(E - E_F)^n + \frac{B}{\sqrt{2\pi}C}\exp[-(\frac{E-E_1}{\sqrt{2}C})^2]$ as shown in Fig. 3 (f) and Table II. The exponents of n are universally estimated to be $\sim 1.3 - 1.6$ by using this function at low temperature of CuIr₂S₄, independent of the gaussian contribution, namely the surface contribution. Therefore, we can safely conclude that, while the hump near E_F is the surface contributions, the in-gap state with the power law function $A(E - E_F)^n$ with $n \sim 1.3 - 1.6$ is derived from the bulk and is responsible for the VRH transport, $\rho \propto \exp[-(T/T_0)^{1/2}]$ (or $\propto A'\exp(-E_a/k_B T) + B'\exp[-(T/T_0)^{1/4}]$).

In the situation forming *softgap* due to electron-electron Coulomb repulsion of Efros-Shklovskii type, the spectral function is usually characterized by $A(E - E_F)^2$ dependence. [22, 39] However CuIr₂S₄ has complicated three-dimensional charge order and has *hardgap* ~ 0.09 eV. Probably, some disorder in the charge-ordered state is the origin of the in-gap spectral feature and the VRH transport. Recently based on transport measurements of Ca_{2-x}Sr_xRuO₄, Nakatsuji *et al.* proposed that the hopping exponent of $\alpha \sim 1/2$ is universal feature of the disordered Mott system close to the metal-insulator transition and reflects the emergence of disorder-induced localized electronic states in the Mott-Hubbard gap. [1]

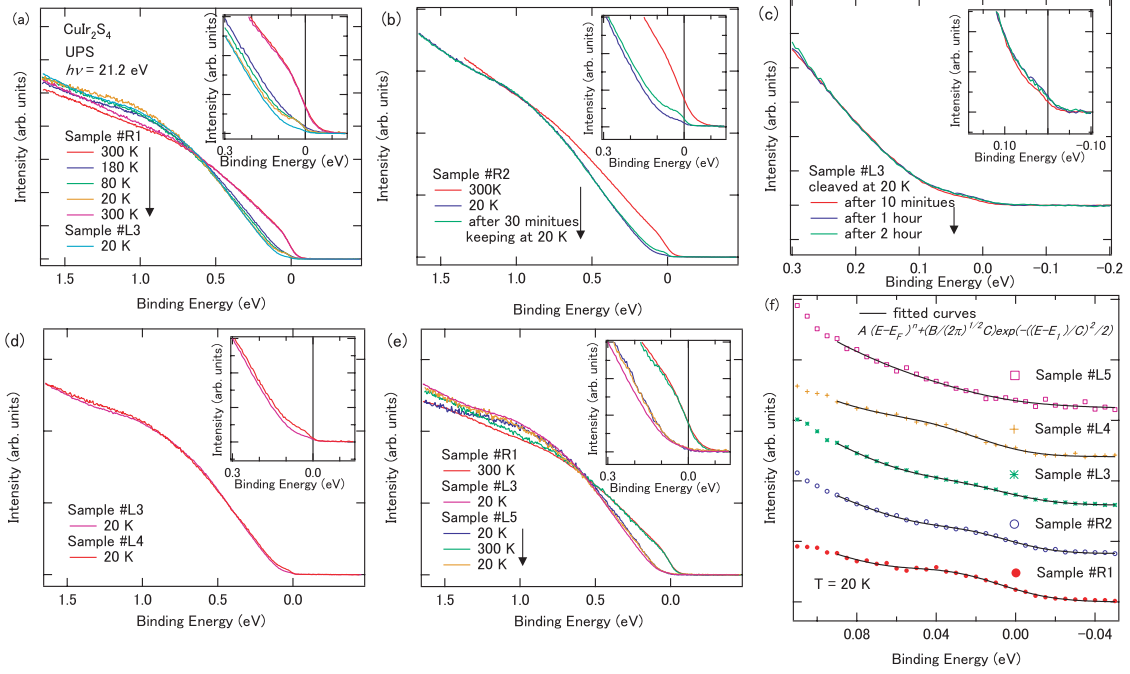


FIG. 3: (Color online) UPS data of CuIr₂S₄ taken at various temperatures and for various samples. (a)-(e) Insets are the expanded spectra near E_F . The arrows denote the order of the measurements. (f) Near E_F region of UPS data for CuIr₂S₄ taken at 20 K. The solid curves indicate the fitted results with model functions $A(E - E_F)^n + \frac{B}{\sqrt{2\pi C}} \exp[-(\frac{E-E_1}{\sqrt{2C}})^2]$.

TABLE II: Best fit parameters of the model function $A(E - E_F)^n + \frac{B}{\sqrt{2\pi C}} \exp[-(\frac{E-E_1}{\sqrt{2C}})^2]$ for the spectra of sample #R1, #R2, #L3, #L4, and #L5 of CuIr₂S₄. The spectra are normalized using integrated intensity up to 0.09 eV.

Function : $A(E - E_F)^n + \frac{B}{\sqrt{2\pi C}} \exp[-(\frac{E-E_1}{\sqrt{2C}})^2]$				
Sample (20 K)	n	B	C (eV)	E_1 (eV)
#R1	1.4 ± 0.2	0.38 ± 0.03	0.03 ± 0.01	0.03 ± 0.01
#R2	1.3 ± 0.1	0.22 ± 0.03	0.02 ± 0.01	0.02 ± 0.01
#L3	1.5 ± 0.2	0.23 ± 0.03	0.02 ± 0.01	0.02 ± 0.01
#L4	1.4 ± 0.1	0.30 ± 0.03	0.03 ± 0.01	0.04 ± 0.01
#L5	1.6 ± 0.2	0.24 ± 0.03	0.04 ± 0.01	0.03 ± 0.01

The presence of some kind of disorder such as coexisting metallic clusters in the insulating phase, which can be created near the first order MIT, gives a strongly localized state and $\alpha \sim 1/2$. A distinct in-gap state is also observed in UPS of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$. [40]

Furthermore, $n \sim 1.3 - 1.7$ for CuIr_2S_4 is rather small compared to the expected value ~ 2 of Efros-Shklovskii type. The suppressed $n \sim 1.5$ of $A(E - E_F)^n$ is observed in a recent photoemission study on BaIrO_3 , which has a quasi-one-dimensional structure with Ir_3O_{12} trimers and also shows a charge-density wave transition. [41] The exponent of $n = 1.5$ for BaIrO_3 is attributed to the strong influence of electron-magnon interaction. The traveling dimer conduction in low temperature phase of CuIr_2S_4 is proposed in Ref. 18. All Ir^{4+} holes at low temperature fall in the xy orbitals and form the dimers along the (110) [or (-110)] chains. [24] When the Ir^{4+} - Ir^{4+} dimer bonds are very strong and the system has good one dimensionality, single hole hopping from an Ir^{4+} - Ir^{4+} dimer to a neighboring Ir^{3+} site along the (110) chain may be suppressed. Instead, paired hole hopping (bipolaronic hopping) of an Ir^{4+} - Ir^{4+} pair along the (110) chain is favored as shown in Fig. 4. The paired hole conduction may have quasi-one-dimensional and bipolaronic features in the (110) or (-110) chains even in the three dimensional lattice. Actually, the UPS line shapes of CuIr_2S_4 across the MIT resemble those of a bipolaronic material Ti_4O_7 . [42] The spectral weight in the insulating phase of Ti_4O_7 also obeys the power-law function $A(E - E_0)^n$ with $n \sim 2$. Moreover, even in the metallic phase, the both spectra of CuIr_2S_4 and Ti_4O_7 show weak Fermi edges and broad peaks at ~ 0.75 eV, around which most of spectral weights are distributed. Such broad feature is commonly interpreted as the incoherent part of the spectral function accompanying the quasi-particle excitations around E_F . Probably, the fluctuation of the dimerization may survive at high temperature metallic phase.

The temperature dependence of the UPS spectra across the MIT is briefly summarized as follows. The $-\text{Ir}^{3+}$ - Ir^{3+} - Ir^{4+} - Ir^{4+} - charge ordering and Ir^{4+} - Ir^{4+} dimerization along the (110) or (-110) chains cause the *hardgap* opening of ~ 0.09 eV, which also manifests in previous studies. [27, 31, 33, 35] On the other hand, the peculiar in-gap state, which shows the power-law behavior with exponent $n \sim 1.3 - 1.7$, gives the anomalous hopping conductivity at low temperature.

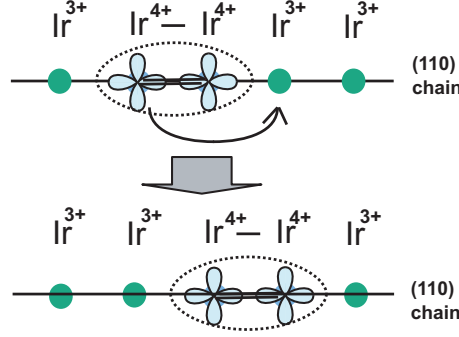


FIG. 4: (Color online) Hopping of holes between an Ir^{4+} - Ir^{4+} dimer and a neighboring Ir^{3+} site along the (110) or (-110) chains. The dimer moves without reducing the number of Ir^{4+} - Ir^{4+} bonds.

B. Photo-excitation effects

We have also studied photo-excitation effects on the near- E_F UPS spectra. No spectral weight increase at E_F was observed for any sample surfaces by visible light irradiation from the Nd:YAG laser up to 5 mJ/pulse (8.5×10^{16} cm²photons/pulse) (See, Fig. 5), indicating that the $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge ordered gap in the insulating phase is very robust against photo-excitation across the band gap. On the other hand, the present visible light irradiation also gives the reduction of the resistance similar to those reported in the x-ray irradiation measurements [Fig. 5 (i)]. The weak irradiation up to 1 mJ/pulse (1.7×10^{16} cm²photons/pulse) gives no spectral change near E_F [Fig. 5 (a)-(e)]. On the other hand, the hump of the in-gap states was decreased by rather strong irradiations of $\sim 3 - 5$ mJ/pulse [Fig. 5 (f)-(h)]. The strong irradiation may cause redistribution of charge at the surface states.

It has been suggested that the long-range charge ordering is destroyed by the x-ray. [25, 26] Probably, the visible light irradiation destroys only the phase of $-\text{Ir}^{3+}-\text{Ir}^{3+}-\text{Ir}^{4+}-\text{Ir}^{4+}-$ chains in the xy plane of spinel. When the Ir^{4+} - Ir^{4+} dimers in the xy chains are shifted to the neighboring sites by the irradiation, the octamer ordering is destroyed (See Fig. 6). This corresponds to the bipolaronic hopping as discussed in Fig. 4 and can be regarded as a kind of bipolaronic solid-to-liquid transition similar to Ti_4O_7 . [42] This picture is consistent with the recent diffraction study of CuIr_2S_4 at low temperature, [30] indicating that the long range order (octamer order) is destroyed but the dimers are preserved locally after x-ray or electron irradiation. Moreover similar charge ordering as shown in Fig. 6 (b) including

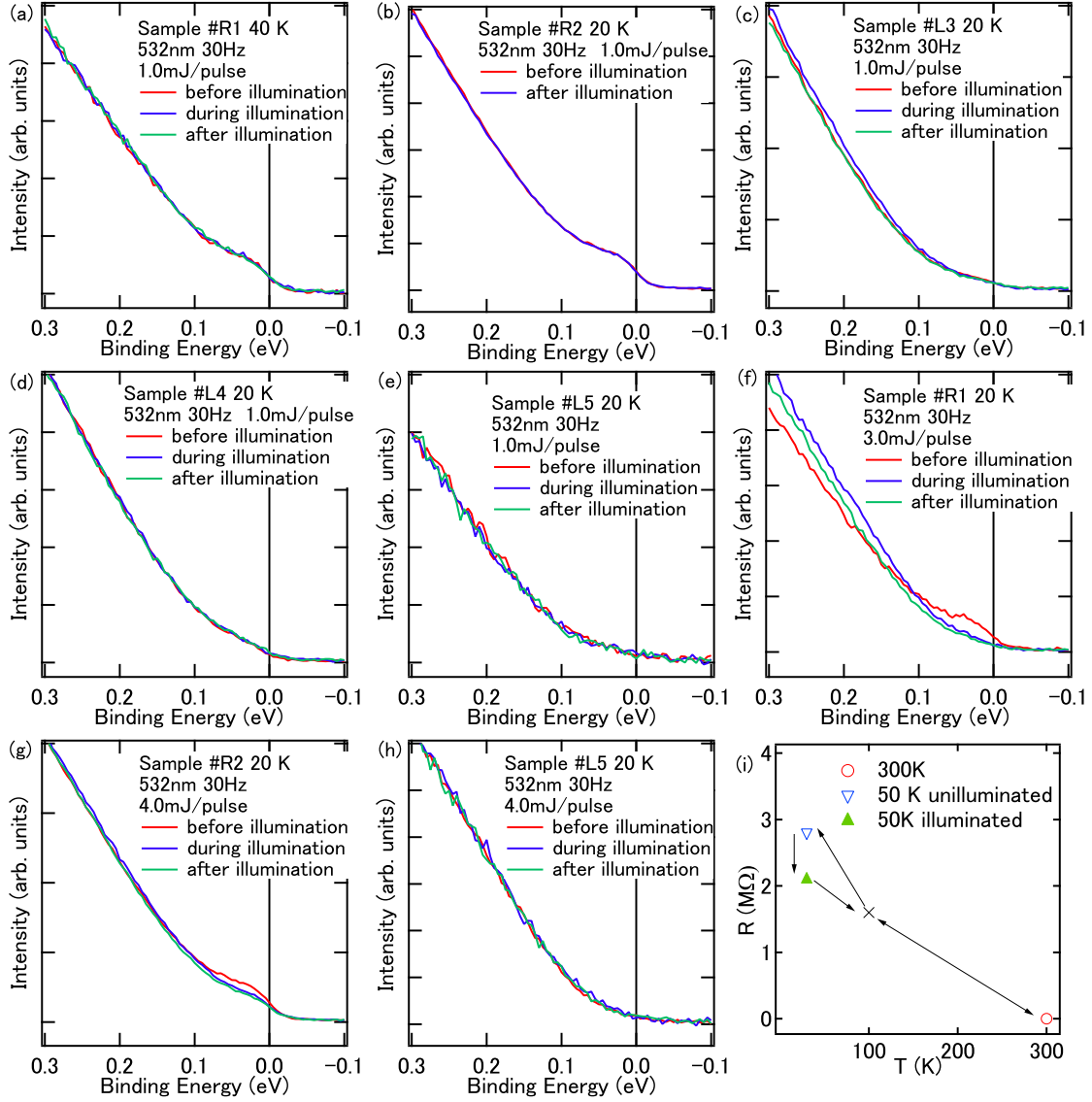


FIG. 5: (Color online) (a)-(h) UPS of CuIr_2S_4 before, during, and after visible light irradiation from the Nd:YAG laser (532 nm) for various samples. (i) The resistance taken under the same condition as the photoemission measurements.

$-\text{Rh}^{3+}-\text{Rh}^{3+}-\text{Rh}^{4+}-\text{Rh}^{4+}-$ chains is observed in the structural study of LiRh_2O_4 , which also has Rh sites at the B site of spinel and shows a metal-insulator transition with some lattice distortion. [43]

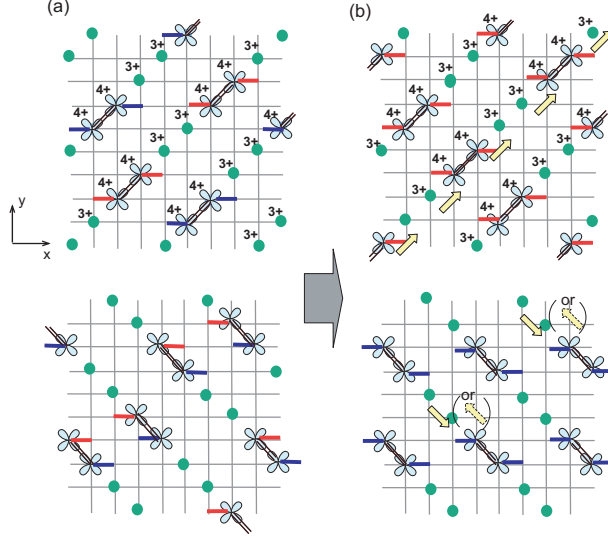


FIG. 6: (Color online) (a) Charge ordering of Ir sites of CuIr_2S_4 sitting in one xy plane. The lower panel is another xy plane $a/4$ below upper panel. The double solid lines denote the Ir^{4+} - Ir^{4+} dimerized bonds. The blue and red lines denote the octamer bonding toward Ir^{4+} in the different planes. (b) When the Ir^{4+} - Ir^{4+} dimers shift by one unit, the octamer ordering is destroyed and another order may appear.

IV. SUMMARY

We have studied the electronic structure of CuIr_2S_4 single crystals using UPS. The UPS data shows the band-gap opening of ~ 0.09 eV and supports the previous report of $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge ordering in the insulating phase. The observed in-gap state at low temperature is consistent with the variable range hopping transport. The UPS measurements under laser irradiation indicate that the $\text{Ir}^{3+}/\text{Ir}^{4+}$ charge disproportionation by the dimer formation is very robust against the photo-excitation but the long-range charge ordering would be destroyed.

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